Determination of Graessley's Relaxation Time in Concentrated Polymer Solutions and Melts

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Synopsis

The method consists of a comparison between experimental data and Graessley's theoretical function of the dependence of viscosity of concentrated polymer solutions and melts on the velocity gradient in a linearized plot using a three-parameter empirical equation. The procedure is objective and allows the use of a computer.

INTRODUCTION

The paper reports a new procedure for the analysis of experimental data on the non-Newtonian viscosity of concentrated polymer solutions and melts using Graessley's theoretical function. According to Graessley's theory[1,2] based on the dynamic equilibrium between the formation and decay of entanglements of macromolecules in flow, the viscosity of a system, η, at a given velocity gradient γ is a function of the concentration of entanglements and time τ_0 needed for their formation, with the concentration of entanglements decreasing with increasing velocity gradient. The theory gives the dependence of η/η_0, which expresses the relative decrease in viscosity (η_0 is viscosity at $\gamma = 0$) on the dimensionless parameter $p = \tau_0\gamma/2$. For a monodisperse polymer the dependence is reported in the form of an explicit relation; for various polydispersities of molecular weights tabulated values are available.[2]

The time constant τ_0 (relaxation time) is a characteristic of the non-Newtonian behavior of a system and a criterion of viscoelasticity, and depends on the structure of macromolecular entanglements. Usually, it is determined by comparing the plot of experimental data log η vs. log γ with the theoretical dependence log (η/η_0) vs. log p using the horizontal displacement needed for them to coincide.[3,4] The value of η_0 can be determined from the vertical displacement. These graphic methods are not too exact, however, because visual evaluation of the best fit of these plots, especially if the range of the gradients is narrow, is not unambiguous as a rule. The procedure reported in this study is more objective, allowing the τ_0 and η_0 values to be obtained by computerizing the results.

THE PROPOSED METHOD

In our procedure experimental data are compared with Graessley's theoretical function in a linear plot by means of a modified three-parameter empirical equation, formerly used in the evaluation and comparison of the

non-Newtonian dependence of intrinsic viscosity of polymer solutions on the velocity gradient under various conditions.[5-12] We found that this equation in the form

$$\eta = \eta_x \left[1 - \gamma/(a\gamma + b)\right] \qquad (1)$$

(where η_x, a, and b are parameters of the equation) may be employed within a wide range of medium and high velocity gradients also for the absolute viscosity of concentrated solutions and melts. The parameter η_x equals viscosity at $\gamma = 0$ and, as is shown below, will be used as an adjustable parameter. The parameter a is related with the limiting viscosity value, η_∞, at $\gamma = \infty$ according to

$$a = \eta_x/(\eta_x - \eta_\infty) \qquad (2)$$

Since the dependence of viscosity on the velocity gradient has a point of inflexion (Fig. 1), and eq. (1) represents hyperbolas monotonically decreasing to the limit, the dependence cannot—like dilute solutions—be used to describe the region of low velocity gradients from the very beginning, where the viscosity is usually constant (plateau of the first Newtonian region) or varies very little, down to the point of inflexion. If the real viscosity value at $\gamma = 0$ is substituted for η_x (i.e., $\eta_x = \eta_0$), the equation somewhat fails, even in the region beyond the point of inflection (Fig. 2, curve 1). This shortcoming has been removed by replacing η_x with η_0^+, which corresponds to the optimal plot of experimental points through an empirical curve from
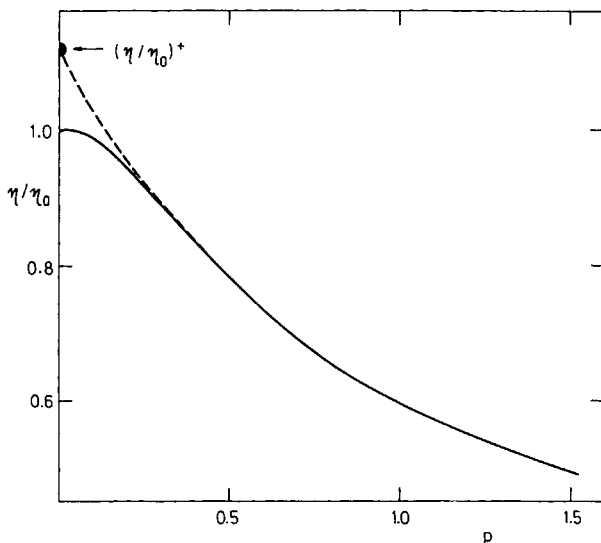

Fig. 1.   Graessley's theoretical dependence of η/η_0 on parameter p for $M_w/M_n = 1.09$. Broken line: optimal plot of the theoretical dependence through empirical function (6) in the region beyond the point of inflexion (cf. Table II).
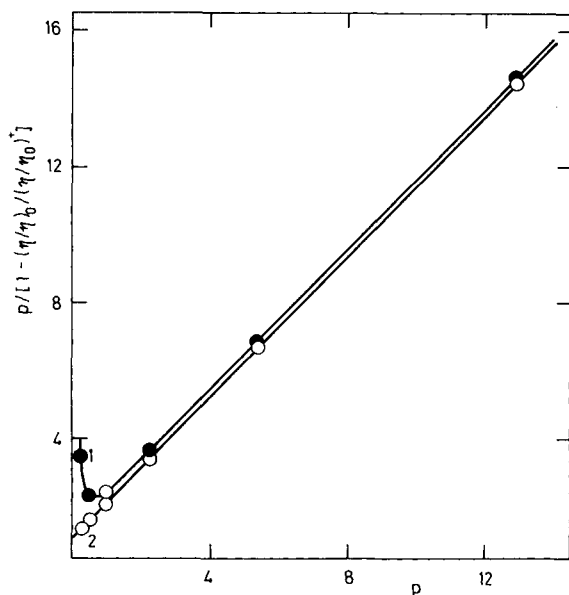
Fig. 2. Plot $p/[1 - (\eta/\eta_0)/(\eta/\eta_0)_x]$ vs. p for Graessley's theoretical function in Figure 1: (●) $(\eta/\eta_0)_x = 1$; (○) $(\eta/\eta_0)_x = (\eta/\eta_0)^+ = 1.117$.

the point of inflexion to higher velocity gradients ($\eta_x = \eta_0^+ > \eta_0$). Equation (1) thus modified,

$$\eta = \eta_0^+ [1 - \gamma/(a\gamma + b)], \tag{3}$$

very adequately expressed the gradient dependence of viscosity, starting already from the point of inflexion. Its rearrangement gave the relation

$$\gamma/(1 - \eta/\eta_0^+) = a\gamma + b \tag{4}$$

according to which the plot $\gamma/(1 - \eta/\eta_0^+)$ vs. γ was linear, with the slope a and the intercept b; η_0^+ was obtained by the optimization of this plot (Fig. 2, curve 2).

Graessley's theoretical dependence, η/η_0 vs. p, also has an inflection. If we want to describe it by eq. (1), the parameter $(\eta/\eta_0)^+ = \eta_0^+/\eta_0 > 1$ must be introduced, so that

$$\eta/\eta_0 = (\eta/\eta_0)^+ [1 - \gamma/(a'\,\gamma + b')] \tag{5}$$

After rearrangement and substitution for $\gamma = 2p/\tau_0$, the relation

$$p/[1 - (\eta/\eta_0)/(\eta/\eta_0)^+] = a'p + b'\,\tau_0/2 \tag{6}$$

is obtained. The reference value $(\eta/\eta_0)^+$, slope a', and intercept $b'\tau_0/2 =$

q are obtained by employing a similar procedure as in the treatment of experimental results, i.e., by optimization of the linear dependence $p/[(1 - (\eta/\eta_0)/(\eta/\eta_0)^+]$ vs. p. Table I gives the $(\eta/\eta_0)^+$, a', and q values obtained by optimization of the plot of tabulated Graessley's theoretical data[2] using relation (6) for various widths of molecular mass distribution. It can be seen that the accuracy of approximation of the theoretical function by means of an empirical equation is very good (Table II). As the theory is based on the assumption that the residual viscosity of solution or melt at $\gamma = \infty$ is zero ($\eta_\infty = 0$), i.e., the system is completely deformable, and viscosity of the solvent is negligible, in the case of an ideal approximation of the theoretical function by the empirical equation the parameter a would be unity. Due to these dependences not being completely identical, the a values thus obtained slightly depart from unity.

Coincidence of the curves expressed in terms of the empirical equation (1) for experimental points and of eq. (5) for the theoretical function assumes equality of the constants $a = a'$ and $b = b'$. If the parameters q and b are known, the relaxation time can be expressed by

$$\tau_0 = 2q/b \tag{7}$$

For polymer solutions, and sometimes also for melts with a lower molecular mass, the η_∞ values are sometimes nonzero. In such case the parameter a in eq. (1) is higher than unity. The conditions for experimental results and the theoretical function may be unified[13] by expressing the relative decrease in viscosity in eq. (4) at $a = 1$ through $(\eta - \eta_\infty)/(\eta_0^+ - \eta_\infty)$ instead of using η/η_0^+ according to

$$\gamma/[1 - (\eta - \eta_\infty)/(\eta_0^+ - \eta_\infty)] = \gamma + b \tag{8}$$

The parameter b required for the calculation of τ_0 can then be obtained as an intercept of the linear plot $\gamma/[1 - (\eta - \eta_\infty)/(\eta_0^+ - \eta_\infty)]$ vs. γ, or better, without the necessity of knowing η_∞, from the linear plot $\gamma/(1 - \eta/\eta_0^+)$ vs. γ by dividing the obtained intercept $b\eta_0^+/(\eta_0^+ - \eta_\infty)$ by the slope $\eta_0^+/(\eta_0^+ - \eta_\infty)$, as ensues from the rearranged eq. (8),

$$\gamma/(1 - \eta/\eta_0^+) = \eta_0^+\gamma/(\eta_0^+ - \eta_\infty) + b\,\eta_0^+/(\eta_0^+ - \eta_\infty) \tag{9}$$

TABLE I
Parameters of Empirical Equation (6) for Graessley's Theoretical Function at Various Polydispersity of Molecular Weights

M_w/M_n	$(\eta/\eta_0)^+$	a	q
2	1.029	1.072	0.552
1.5	1.045	1.072	0.716
1.16	1.072	1.036	1.079
1.09	1.117	1.033	1.119
1	1.242	1.024	1.097

TABLE II
Comparison Between $(\eta/\eta_0)_G$ Values of Graessley's Theoretical Function and $(\eta/\eta_0)_c$ Values Calculated Using Eq. (6)

$M_w/M_n = 2$			$M_w/M_n = 1.09$			$M_w/M_n = 1$		
p	$(\eta/\eta_0)_G$	$(\eta/\eta_0)_c$	p	$(\eta/\eta_0)_G$	$(\eta/\eta_0)_c$	p	$(\eta/\eta_0)_G$	$(\eta/\eta_0)_c$
0.055	0.939	0.936	0.213	0.938	0.939	0.411	0.905	0.905
0.115	0.843	0.853	0.444	0.808	0.802	0.951	0.675	0.671
0.253	0.692	0.713	0.975	0.600	0.604	2.18	0.425	0.428
0.583	0.512	0.519	2.24	0.385	0.388	6.76	0.197	0.195
1.40	0.343	0.327	5.32	0.222	0.218	13.4	0.119	0.119
3.45	0.210	0.194	12.9	0.119	0.119			
8.66	0.120	0.123						

Since the η_0^+ values for experimental data and $(\eta/\eta_0)^+$ for the theoretical function are related by

$$(\eta/\eta_0)^+ = \eta_0^+/\eta_0 \qquad (10)$$

the real viscosity of the polymer system at zero velocity gradient can be calculated by merely dividing both reference values:

$$\eta_0 = \eta_0^+/(\eta/\eta_0)^+ \qquad (11)$$

VERIFICATION OF THE METHOD

The procedure for obtaining τ_0 and η_0 values suggested by us was checked by using results of measurements of the gradient dependence of viscosity of the melt of four polystyrene samples reported by Stratton[14] and treated by the method of displacement of logarithmic plots in a paper by Graessley and Segal.[3] Similarly to these authors, we compared experimental data with the theoretical function calculated for the width of molecular weight distribution with $M_w/M_n = 1.09$.

The parameters a, b, and η_0^+ obtained by optimization of these data according to eq. (2) were caluclated by using relations (7) and (11) to τ_0 and η_0 (Table III). Since the values of parameter a were also close to unity in

TABLE III
Comparison Between the τ_0 and η_0 Values for the Polystyrene Melt[14] Obtained by a Displacement of Logarithmic Plots[3] (I) and by Our Method (II)

Sample	$M \times 10^{-3}$ (g mol^{-1})	$\eta_0 \times 10^{-2}$ (Pa s)	a	b (s^{-1})	$\eta_0 \times 10^{-2}$ (Pa s)		$\tau_0 \times 10^3$ (s)	
					I	II	I	II
S 103	117	29.1	1.02	49.3	25.7	25.8	47	41
S 109	179	112.7	1.004	10.5	109	109	230	230
S 111	217	214	1.0007	6.3	190	190	374	373
S 108	242	289	1.001	3.28	295	289	700	682

this case ($\eta_\infty \doteq 0$), the comparison between experimental data and the theoretical function appeared to be justified. It can be seen that the results are comparable with those obtained by the original Graessley's method.

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